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Reaction Between Thin Gold Wires and Pb-Sn-In Solder (37.5%, 37.5%, 25%), Part B. The "Axial Reaction" of Gold Wires Solder To PbSnIn Solder Mounds, Its Effect On Electrical Resistance And Physical Structure

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February 7, 2011

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Introduction

Here we describe the gold-indium reaction along gold wires soldered at both ends. It begins with the combined radial/axial reaction in the vicinity of the solder mound as seen in metallurgical sections along the axis of the wire. We show that this combined radial/axial reaction has no effect on the resistance of the system, even though it shortens the length of the gold wire while converting it to gold indide. After this radial/axial reaction is complete, a purely axial reaction begins. For thin gold wires (i.e. 38.1µm diameter) the onset of that reaction is strongly correlated with the time at which the linear reaction model predicts the complete consumption of the gold wire inside the solder mounds. This purely axial reaction converts at elevated temperatures the whole wire rapidly to gold indide, and leads to substantial resistance changes and complete distortion of the wire between the solder mounds. The reaction product is $AuIn_2$ everywhere, but both Sn and Pb also are identified everywhere on the surface by Electron Dispersive Spectroscopy.

B.I.) The simultaneous "radial" and "axial" gold-indium reaction at the edge of the solder mounds.

In Part A, figure 7, a radial section through a solder mound was presented. The gold – indium reaction is, however, NEVER completely "radial". The indium diffuses not only radially inside the solder mound to the gold wire, but at the same time proceeds by surface diffusion along the gold wire outside the solder mound, where a radial reaction starting from the surface subsequently occurs to form a "protrusion" or "bull nose" outside the solder mound. Figure 10 shows an axial section through an aged bridge-wire and its solder mounds that reveals this surface diffusion outside the mounds and the concomitant gold indide formation. Since the angle of the interface between gold and gold indide is approximately 45 degrees (see figure 10), one may conclude that the axial rate of surface diffusion is approximately the same as the radial rate of gold-indide formation. Figure 11 shows a top-view of an aged bridge-wire, depicting the diameter of the "bull-nose" formed and the associated shortening of the gold-wire's length.

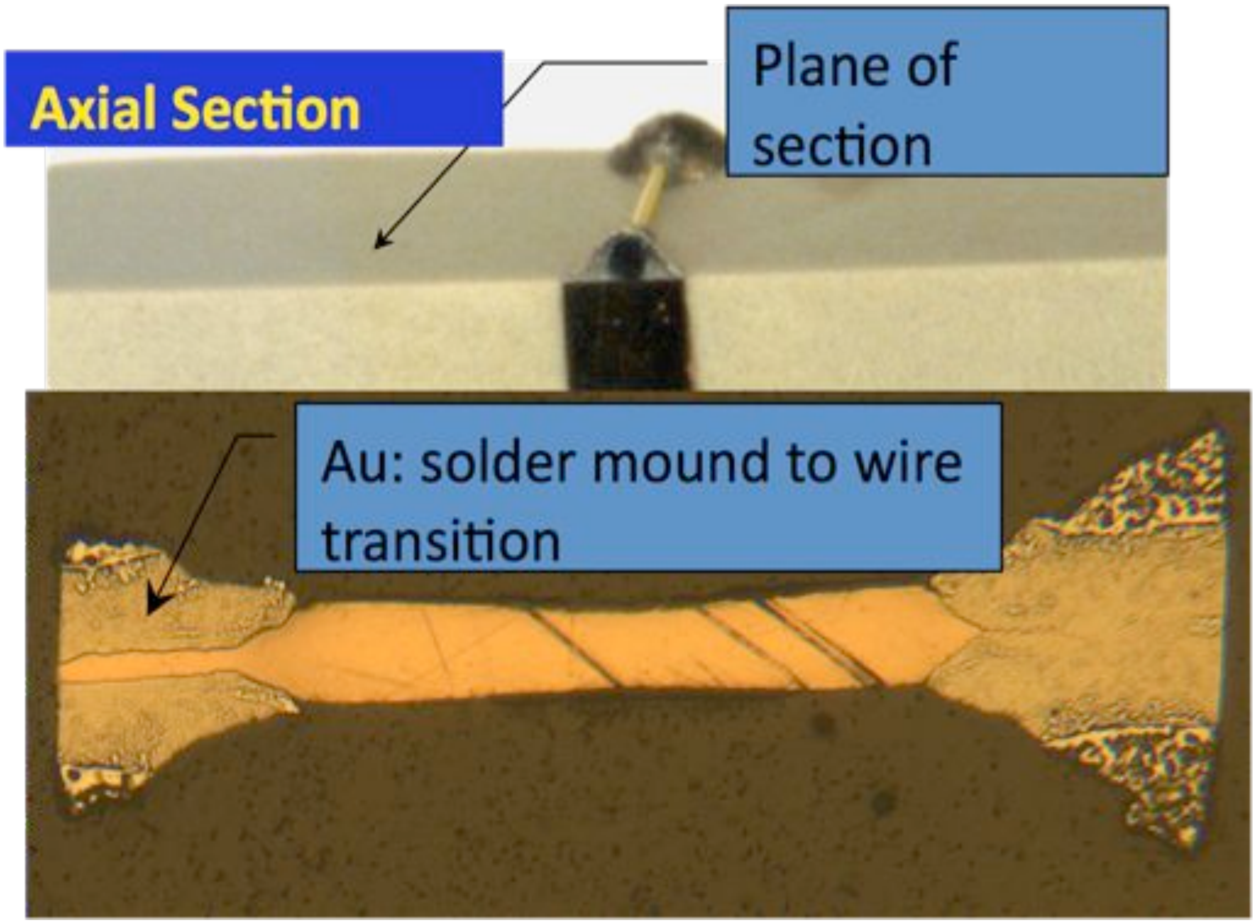


Figure 10. Section along axis of a gold bridge-wire bridge completely converted to gold-indide in the right solder mound, and almost completely in the left mound, on both sides showing the transition from radial to axial reaction. The angle formed at the transition between gold and gold-indide outside the mounds is about 45°. That implies that the radial rate of formation of gold-indide is approximately as fast the movement of indium along the surface of the wire. That has been shown in studies at LLNL to be true at a range of temperatures, implying that the activation energy for surface diffusion is approximately the same as the activation energy for radial gold-indide formation.

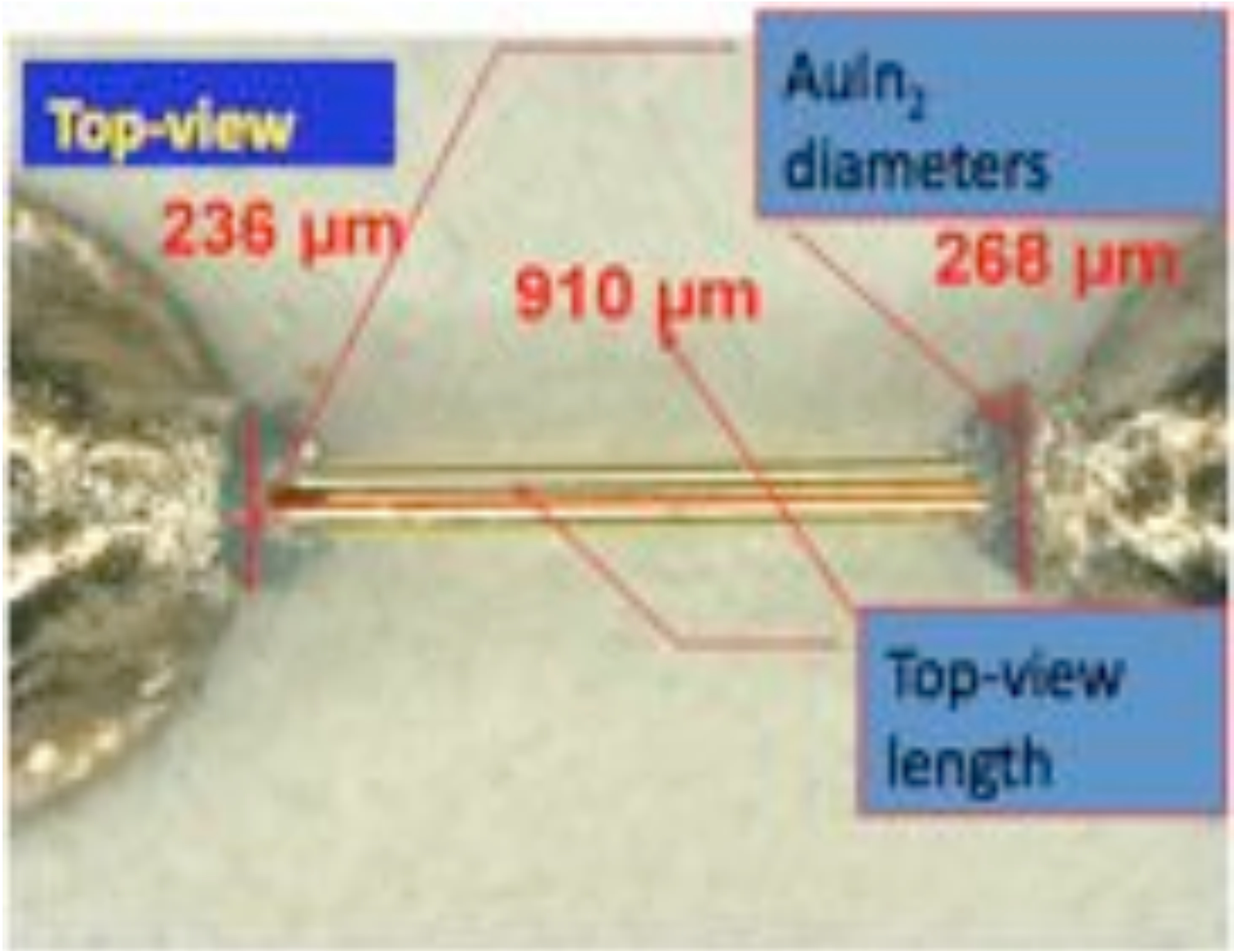
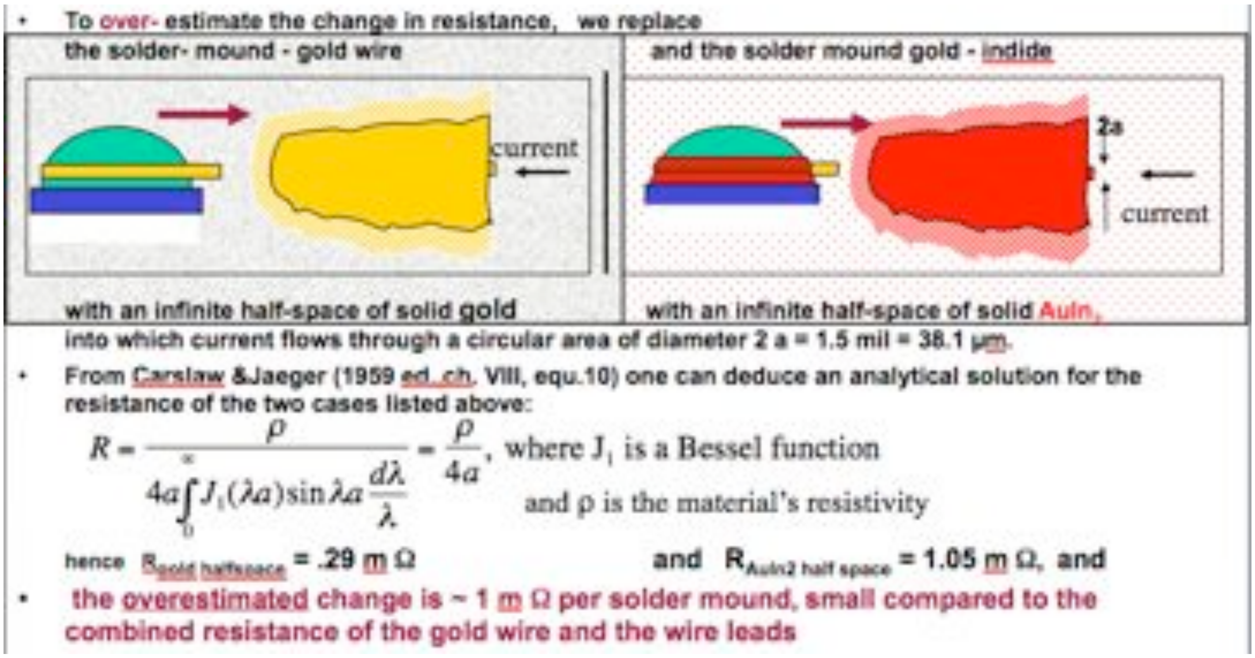


Figure 11. Top-view of a header with a gold-wire of 101.6 µm diameter. The radial reaction has converted the gold wire inside the solder mound. Simultaneously indium has diffused from the solder mound along the surface of the gold wire and converted the wire to gold-indide near the solder mound, in the manner shown in figure 10. A characteristic "bull nose" is thus formed. The diameter of the gold-indide (black) near the solder mounds is 238 and 268 µm, respectively. If the gold-indide created from complete conversion of a gold wire of 101.6 µm diameter were fully dense, and did NOT include any inclusion of other matter, its diameter would be only 208.2 µm. Secondary Electron Microscopy Images (see figures 22 to 25) reveal that the axial reaction product is fibrous, and figure 7 in Part A demonstrates that even inside the solder mound, where the reaction product is formed under pressure, it is NOT fully dense. The gold-wire's length is shortened by this "bull nose" growth.

B.II.) The transition from "radial" to purely "axial" reaction with concomitant resistance change of the gold-wire bridge.

The radial reaction inside the solder mound does NOT cause a resistance change of the bridge, as the calculation below demonstrates:



Even the combined radial/axial reaction near the solder mound forming the "bull nose" does not change the resistance of the bridge. The resistivity of gold-indide (8 µOhmcm [10]) is higher than the resistivity of gold (2.2 µOhmcm), but the increase in volume (a factor 4.2) from gold to gold indide compensates almost exactly.
Nevertheless, substantial increases in resistance were found when a number of headers with 1.5 mil (38.1 µm) diameter gold wires were held at various temperatures at site 300 and monitored continuously over time as shown in figures 12 to 16. (Just one example at each temperature is shown in the figures, there were at least 5).

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[10] Jan , J. P. P., W. B. (1963). "Electrical Properties of AuAl2 AuGa2 and AuIn2." Philos. Mag., 8, 279, 1963. Also CRC Handbook of Electrical Resistivities of Binary Metallic Alloys, Editor Klaus Schroeder, CRC Press, Inc. Boca Raton, Florida

The time at which a rapid increase of the samples' resistance occurred at each temperature was measured, as seen in figures 12 to 16, and the time of these occurrences is plotted in figure 17 in a log-log plot versus the time at which the linear reaction model predicts that the radial reaction has completely consumed the 38.1µm diameter gold wire inside the solder mound. At that time the "bull nose" is also fully formed. There is a strong correlation, albeit with a very wide scatter in the data, particularly at the highest temperature, 120°C. This strong correlation leads to the hypothesis that at this time a different reaction mechanism occurs. It will be discussed in the next section.

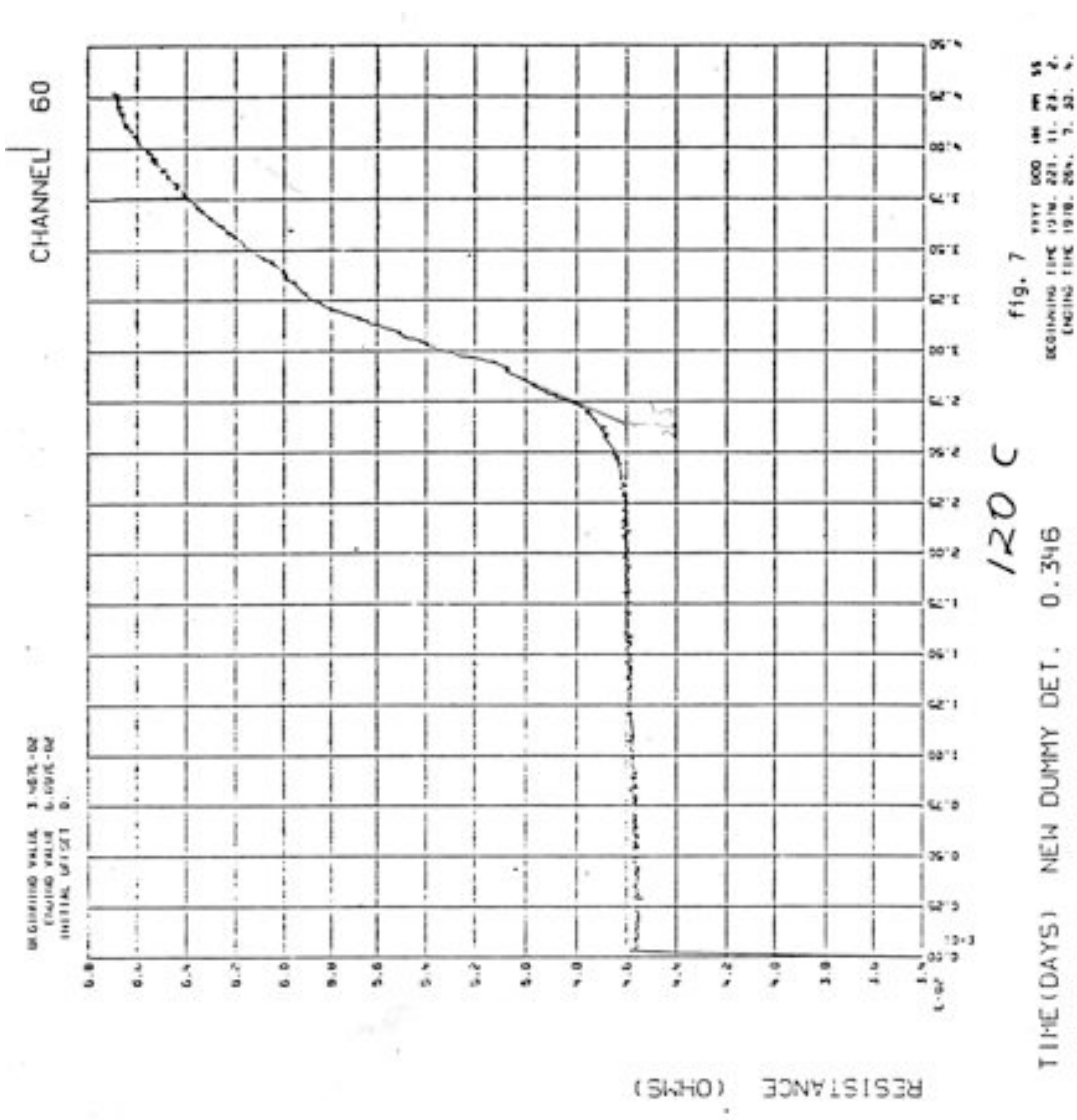

Figure 12. Resistance change of a 1.5 mil gold wire header held at 120°C as a function of time.

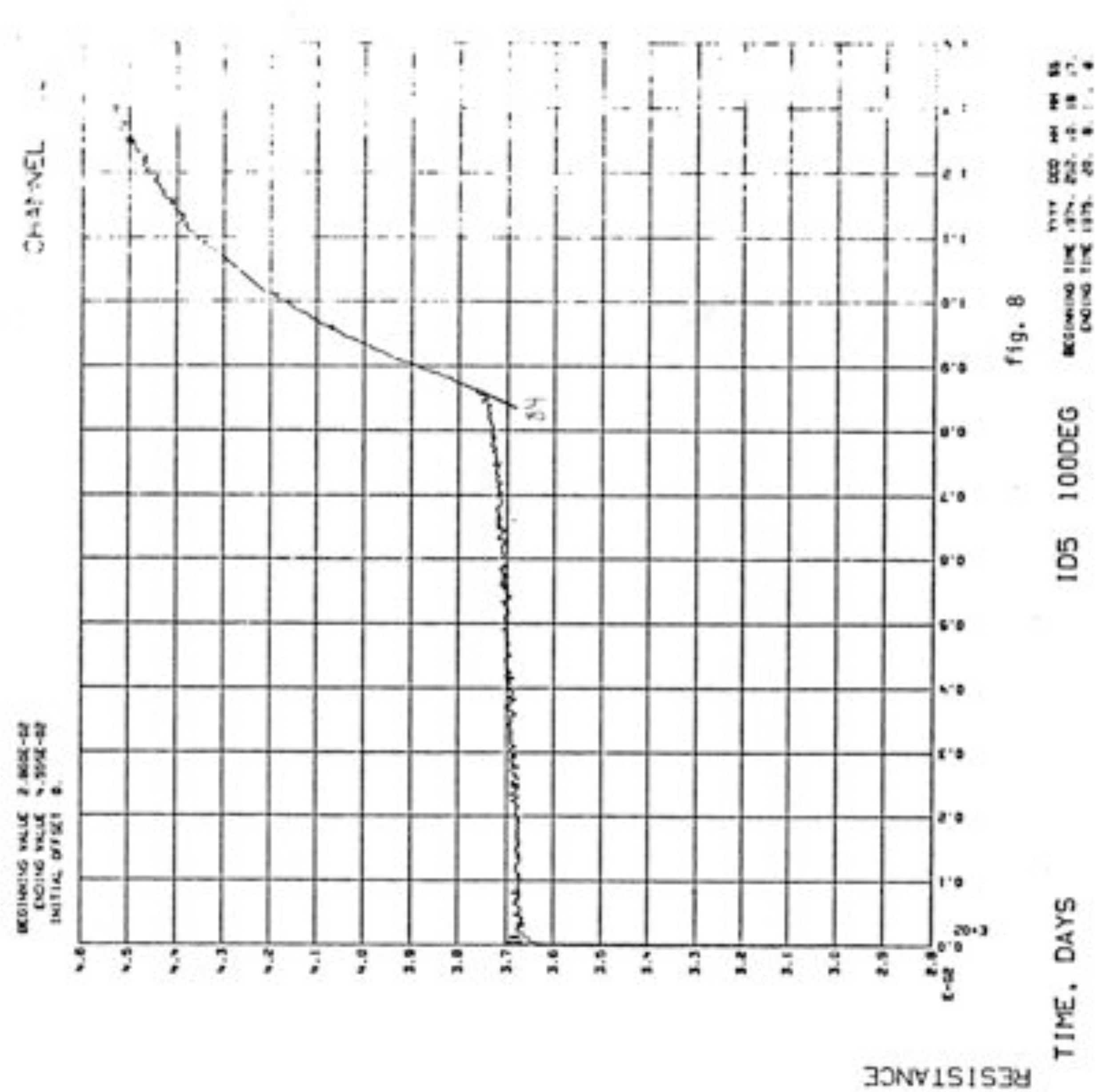

Figure 13. Resistance change of a 1.5 mil gold wire header held at 100°C as a function.

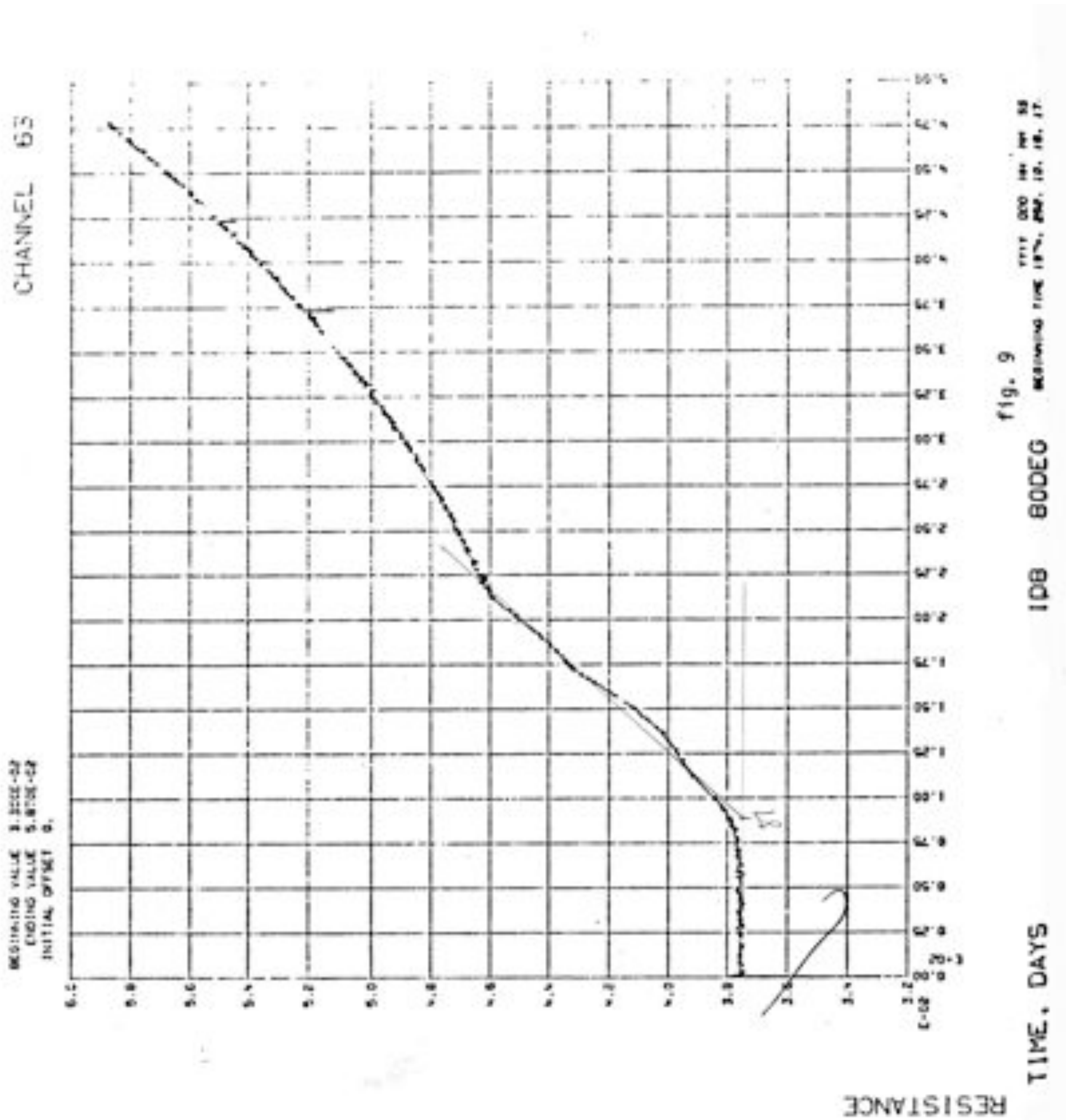

Figure 14. Resistance change of a 1.5 mil gold wire header held at 80°C as a function of time.

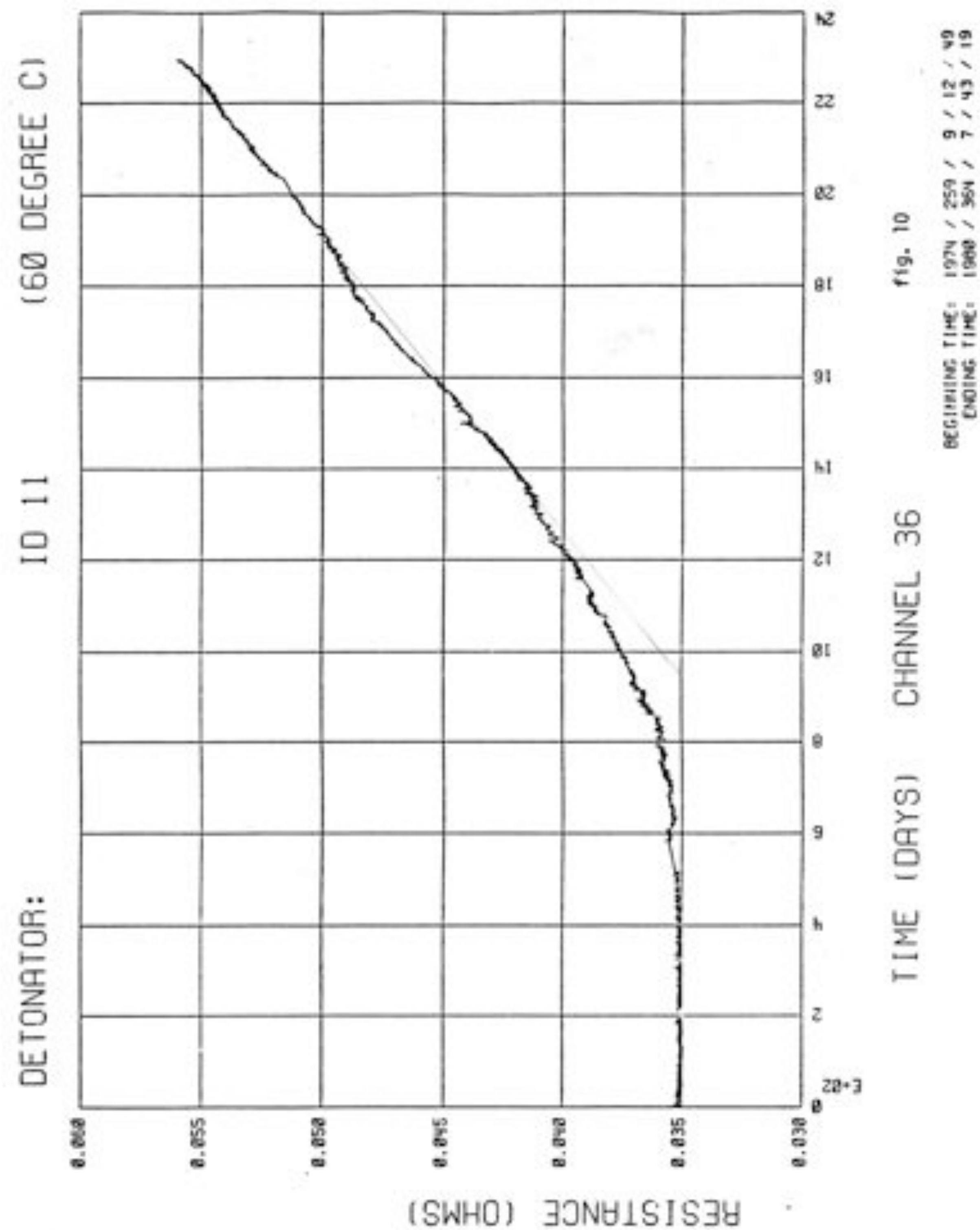

Figure 15. Resistance change of a 1.5 mil gold wire header held at 60°C as a function of time.

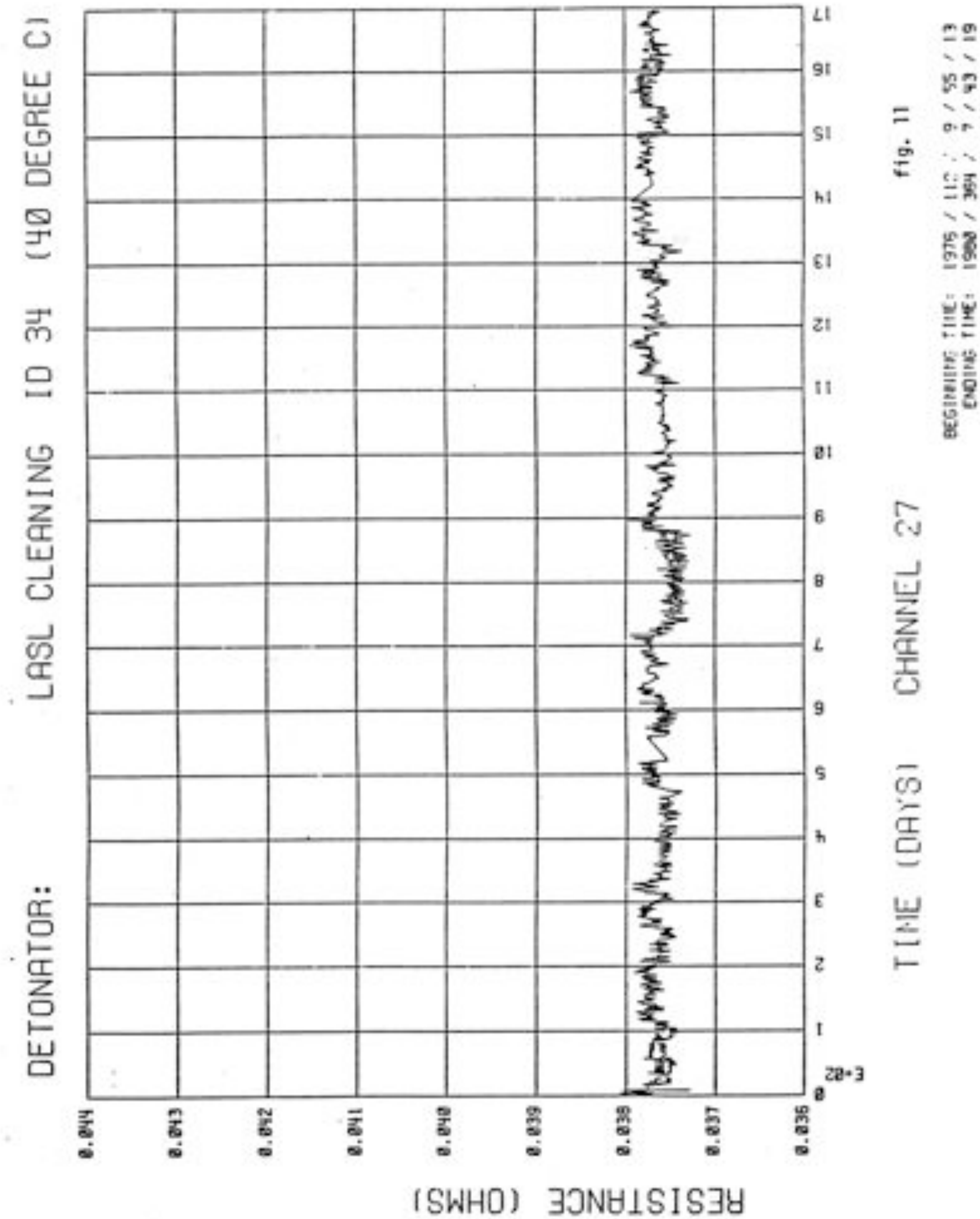

Figure 16. Resistance change of a 1.5 mil gold wire header held at 40°C as a function of time.

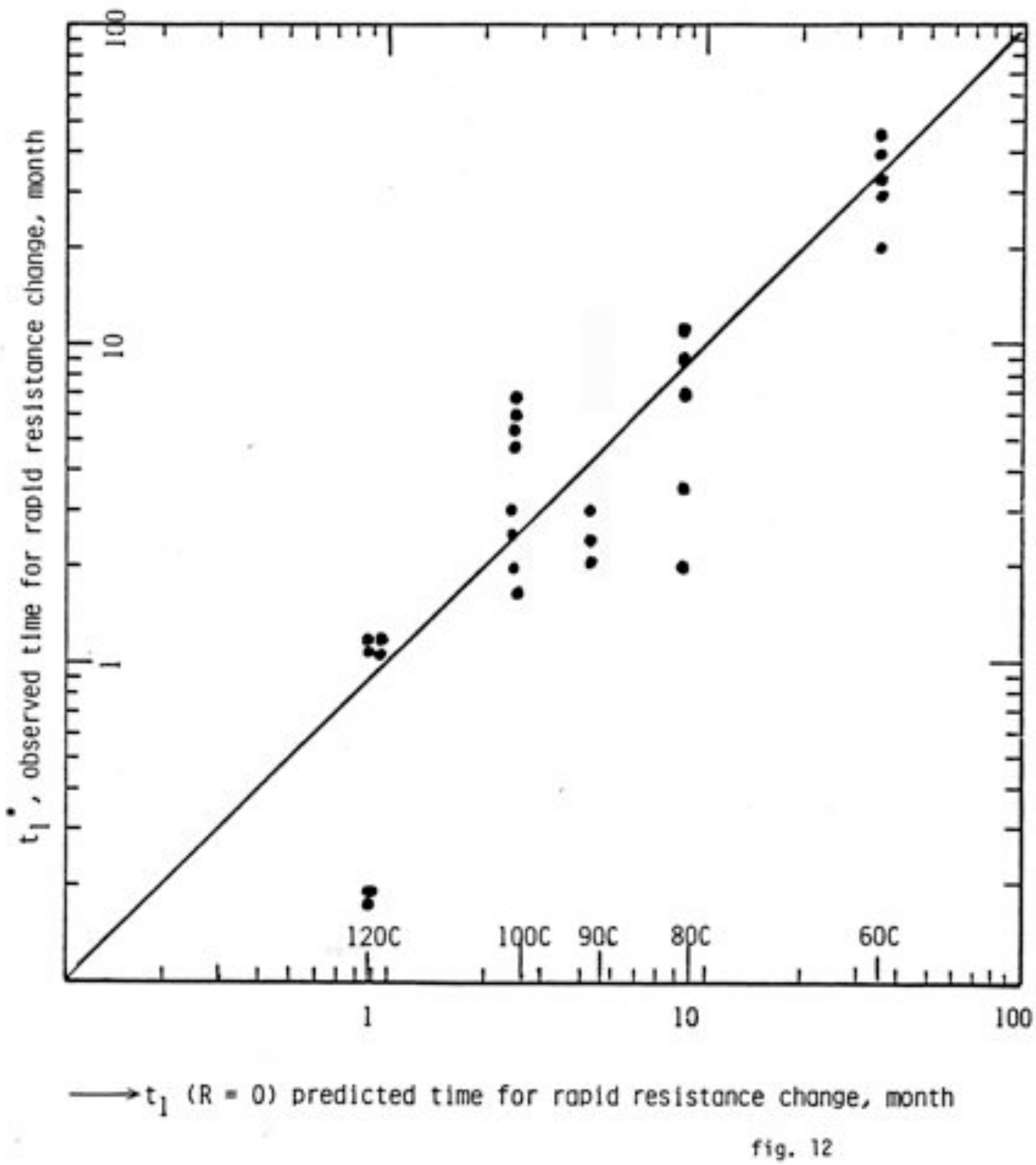

Figure 17. Time at which rapid resistance change of 1.5 mil gold wire headers is observed to start as a function of time at which the linear model predicts total consumption of the gold wire. (Graph modified from earlier version).

B.III.) The "purely axial reaction", rapid resistance increase and structural changes associated with it.

To understand the resistance changes seen in figures 12 to 16, experiments were performed at high temperature (100 and 120 C) in which the structural change in the bridge was observed by time-lapse photography, while the resistance of the bridge was measured simultaneously, see figure 18. As figure 19 illustrates, at the end of such an experiment the bridge consists of the mounds, a stubby protrusion ("bull nose") from each mound, followed by a thinner contorted growth emanating from each "bull nose", and a short section of the remaining gold wire. Figure 20 uses the time-lapse photography and resistance measurements of the experiment depicted in figure 18, and plots the bridge's resistance, the measured length of the remaining gold wire, and the diameters of the "bull nose" as well as that of the "thin axial growth" emanating from the "bull nose" versus the frame number. The thin growth has approximately the same diameter as the gold wire. Since $AuIn_2$'s resistivity is about twice that of gold's, and the volume increase from gold to gold indide is a factor 4.2 (see table 1 of Part A), this thin growth results in substantial increase in length of the material between the solder mounds, accompanied by a corresponding resistance increase. There were 4 frames per hour in the experiment sketched in figure 18; hence the x axis (frame number) can be converted to exposure time. Figure 20 demonstrates that the rapid resistance increase occurs as the thinner growth begins at the end of the "bull nose" at a frame number equivalent to 22 days of exposure at 120°C, a time consistent with the graph in figure 17 that correlates resistance increase with the time the linear model predicts completion of the radial reaction.

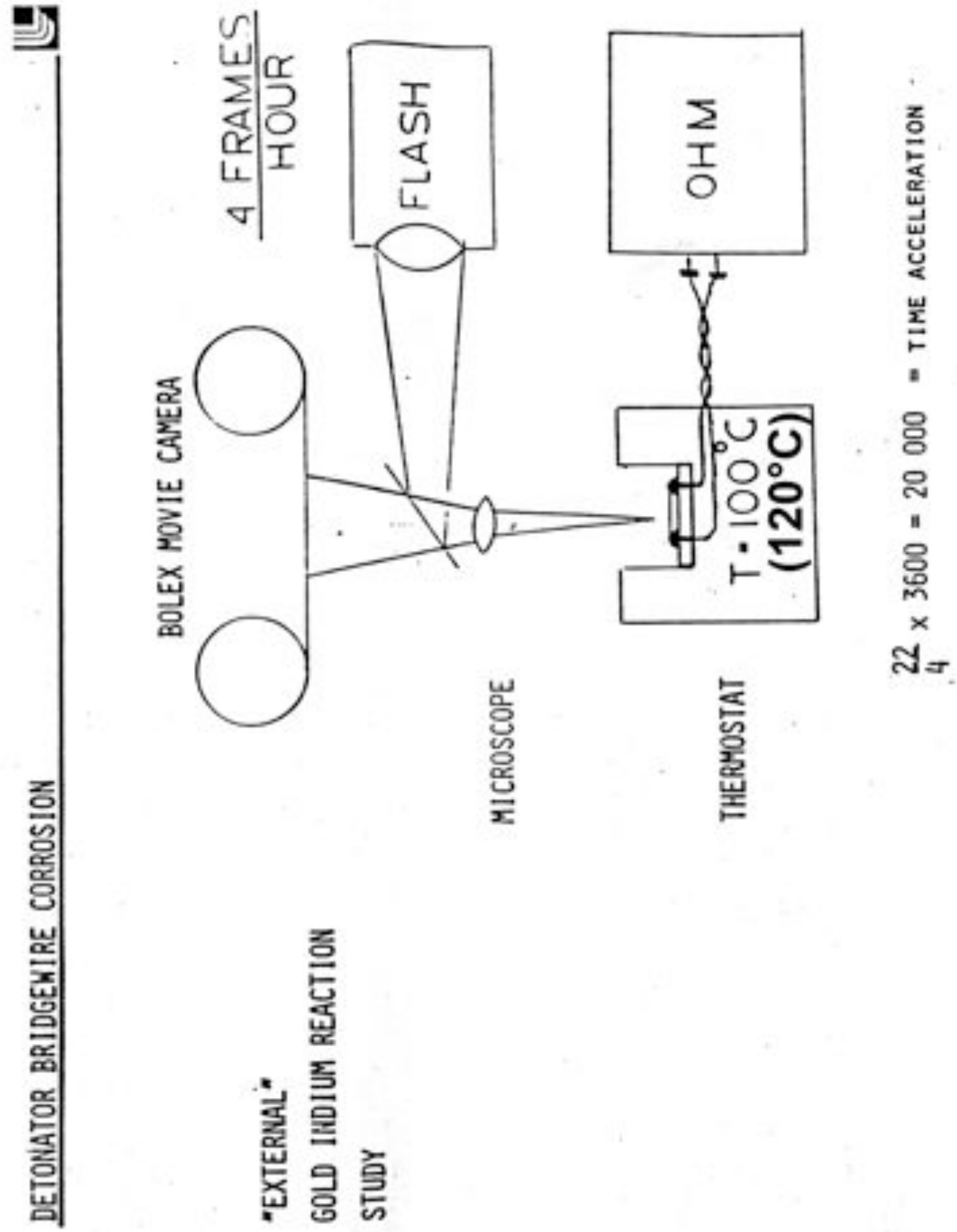

Figure 18: Experimental setup to simultaneously observe structural (i.e. "axial reaction) and resistance changes of soldered 1.5 mil gold wires held at elevated temperature (100 to 120°C)

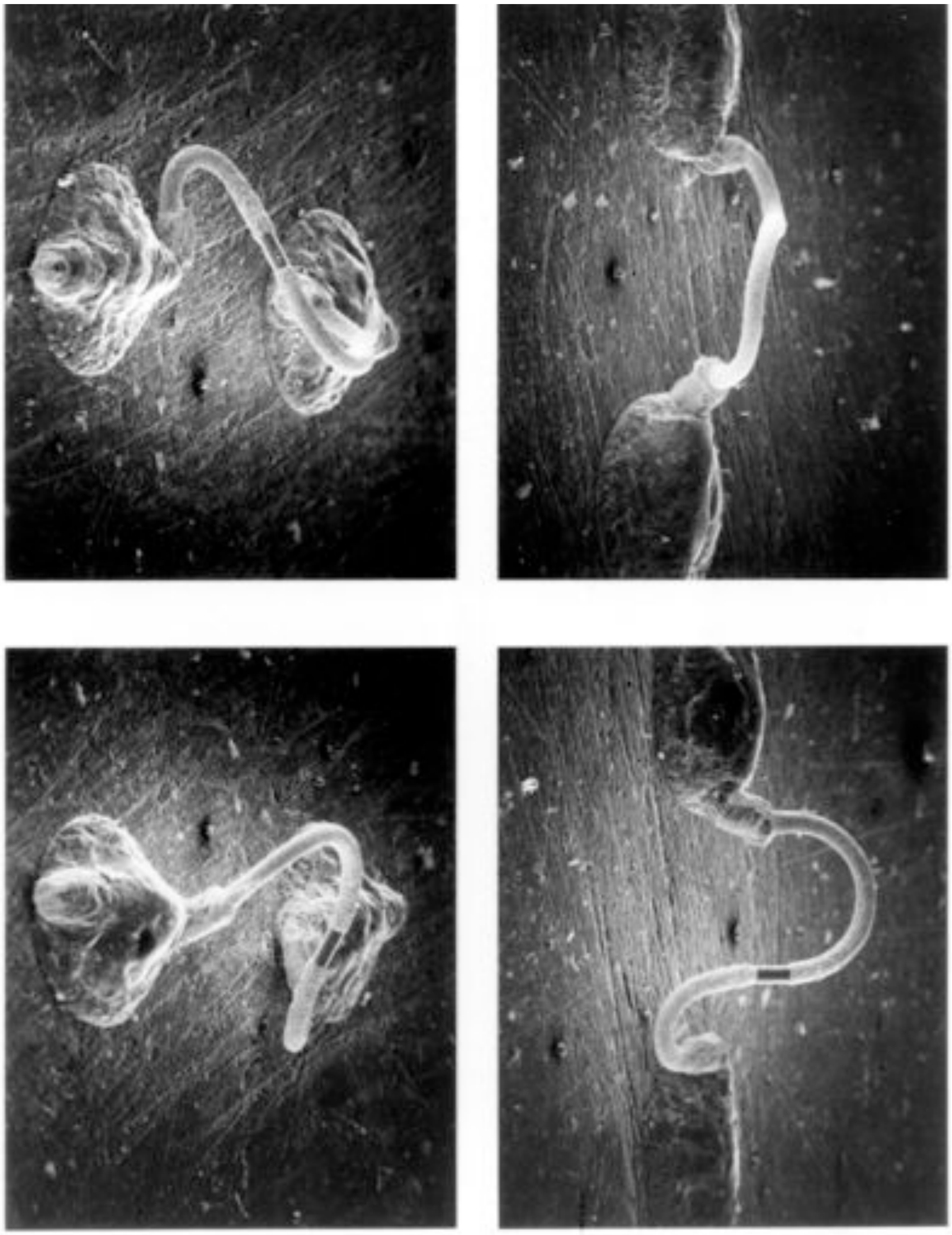

Figure 19. Structural changes of a 1.5 mil held at 120°C for 83 days. 1.) The mounds are deformed: the gold wire's center is pushed up: $AuIn_2$ has four times the volume (-> two times the diameter) of the consumed Au. 2.) A thick $AuIn_2$ protrusion (~3 mil diameter) extends from both sides of the mound. 3.) A thinner (~ 1.5 mil) $AuIn_2$ feature follows the thick $AuIn_2$ protrusions, contorted because each Δl length of Au makes approximately 4 Δl of $AuIn_2$. 4.) The contortion produced a fracture at the mound/wire interfaces. 5.) Very little of the gold wire is left.

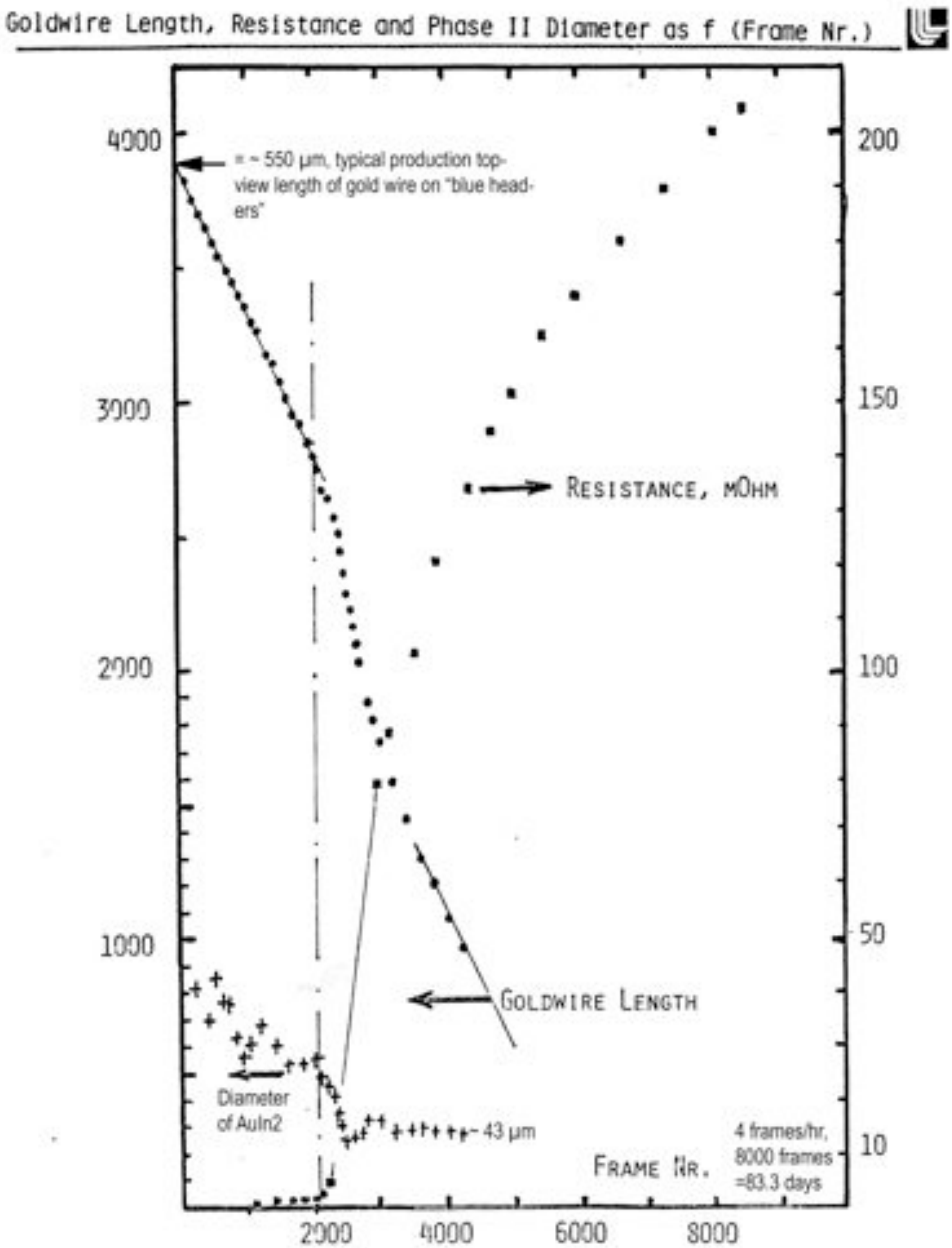

Figure 20. Changes in: gold wire length, diameter of $AuIn_2$ protruding from the mounds, and resistance of a 1.5mil gold wire header held for~83 days at 120°C. Rapid resistance change occurred at ~ 2100 frames, ~ 22 days, consistent with figure 17, where it occurred at ~ 25 days.

B.IV.) Elemental Analysis of the "axial reaction" products.

Figures 21 to 26 show the SEM images and EDS compositional analysis of the axial reaction products. Figure 21 identifies the locations where images and EDS spectra were taken. Images 22 to 26 demonstrate, that the reaction product is $AuIn_2$ everywhere, but surprisingly (most easily visible in figure 26, EDS distribution images of the elements Pb, Sn, In) both Pb and Sn are also present on the surface, albeit in "speckles". In figure 27 the EDS spectra of three calibration alloys, AuIn, $AuIn_2$, and $AuIn_3$ are given for comparison. In figure 23 one sees that "the fracture" at the end of the "bull nose" consists of fibers of gold indide. Gold indide is at room temperature a hard and very brittle material that shatters easily. The stress that can be exerted by the gold wire is small. One has to conclude that at 120°C the diffusion transport indium is sufficiently fast to form new material to relieve the buckling-induced tensile stress occurring at the edge of the mound. However, it is apparent that the transport of elements across the "crack" clearly hindered the gold-indium: the length of the "thin $AuIn_2$ axial growth" emanating from the "bull nose" with the fracture is shorter than from the other bull nose.

Figure 21. Top-view of header aged @ 120°C for ~ 83 days. The black spots with numbers 1 to 4 indicate the locations where elemental analysis was performed by Electron Dispersive Spectroscopy (EDS), see subsequent slides.

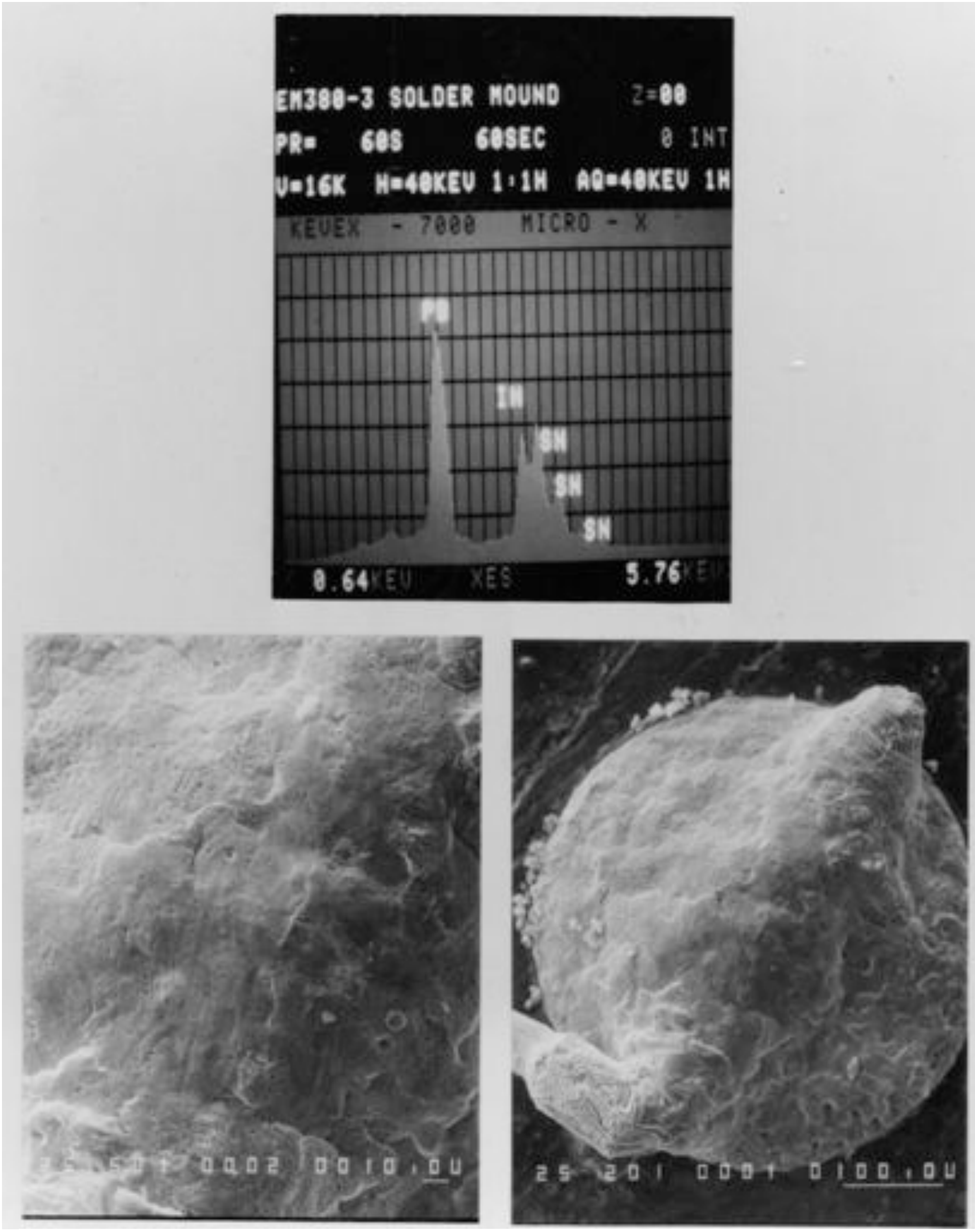

Figure 22. SEM image and EDS spectrum at location 1 on the solder mound indicated in figure 21. The spectrum shows the expected concentration of elements: Pb, Sn, In in the mound.

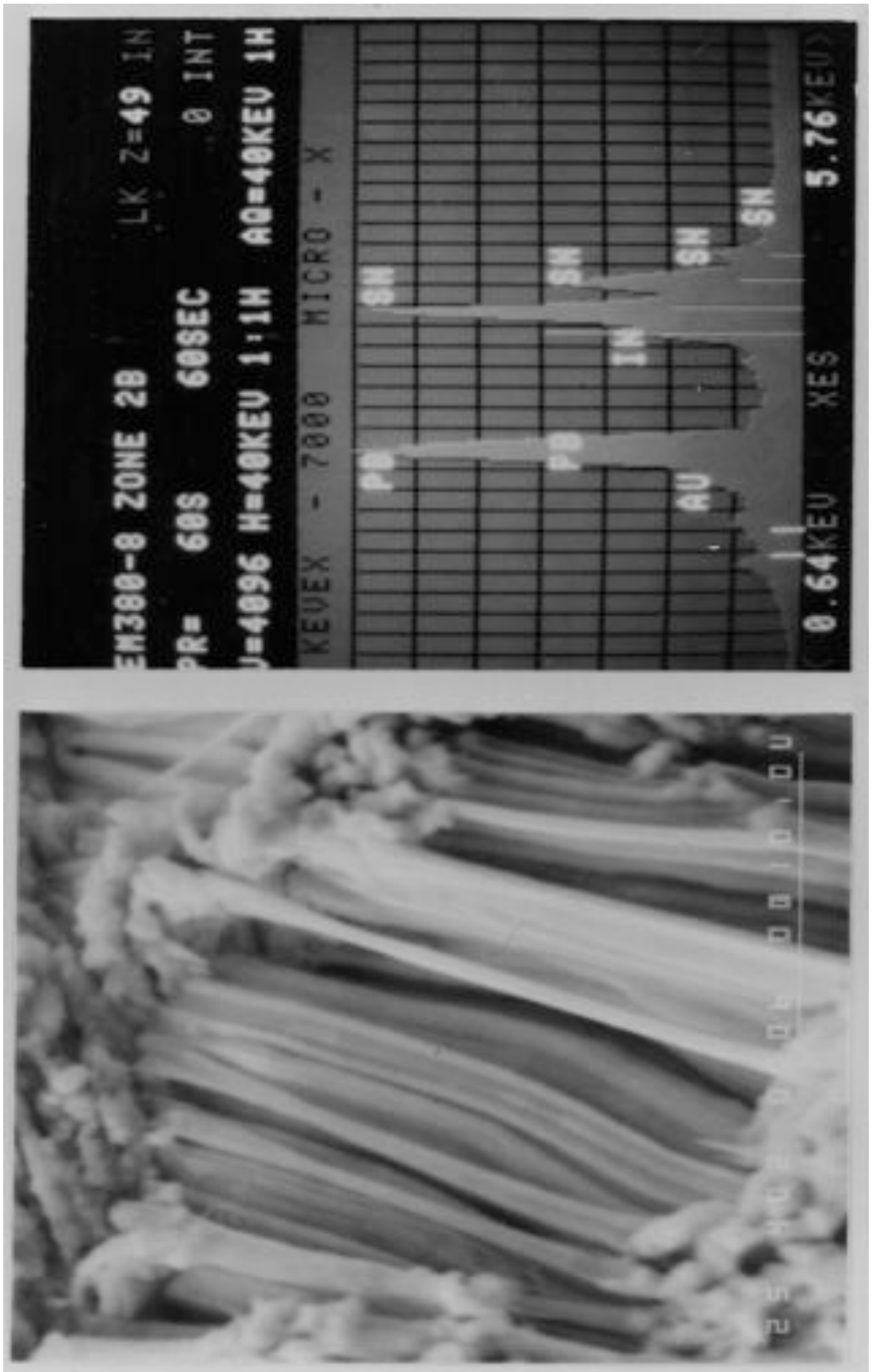

Figure 23. EDS at location "2" in figure 21, i.e. inside the fracture near the solder mound. Clearly both Pb and Sn are "dragged along" as the crack opens. See also figure 26.

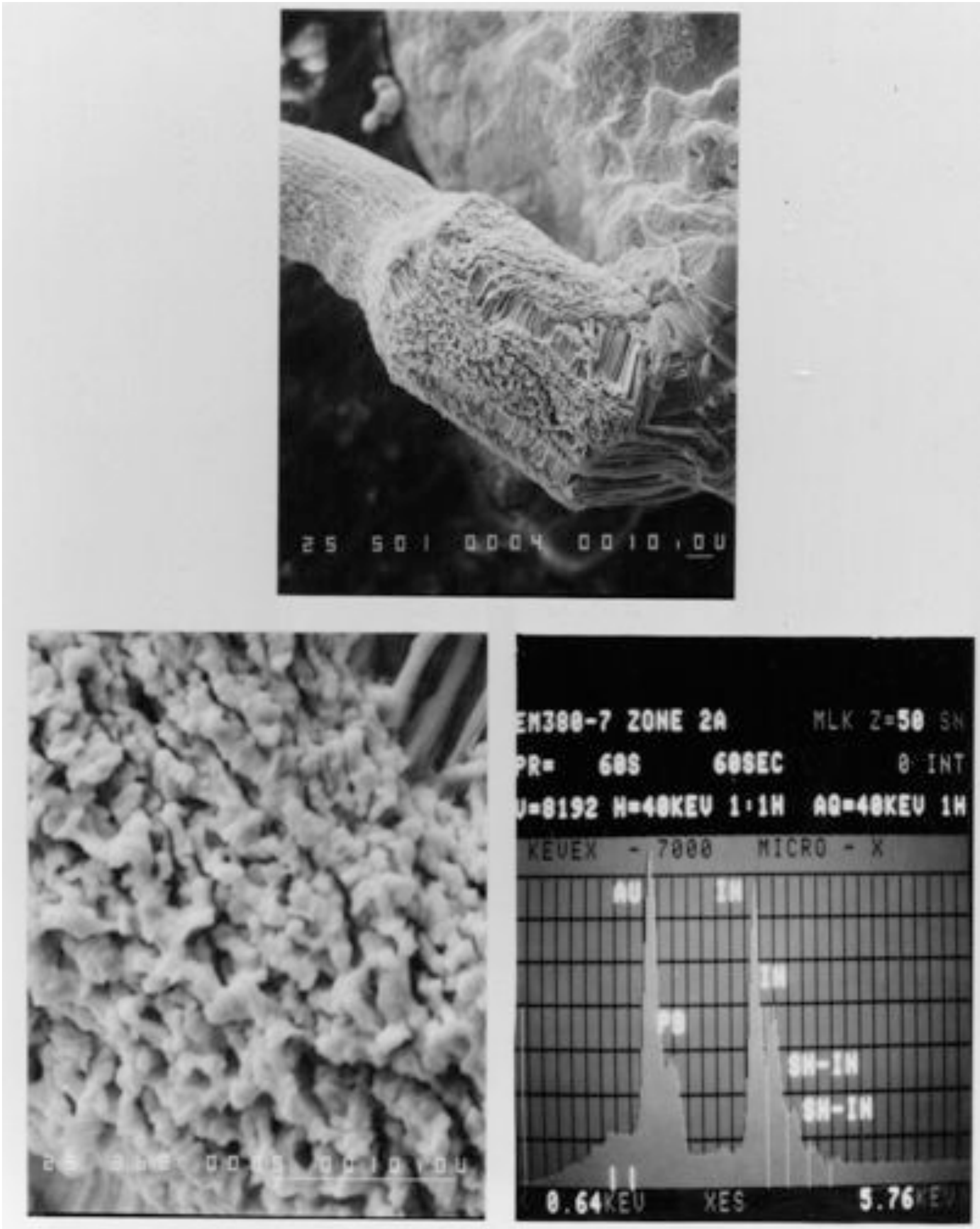

Figure 24. EDS spectrum at location "3" of figure 21, i.e. on the large diameter (~ twice the gold wire's, but clearly not fully dense) "protrusion" emanating from the solder mound. Mostly Au and In are present, with some Pb and Sn.

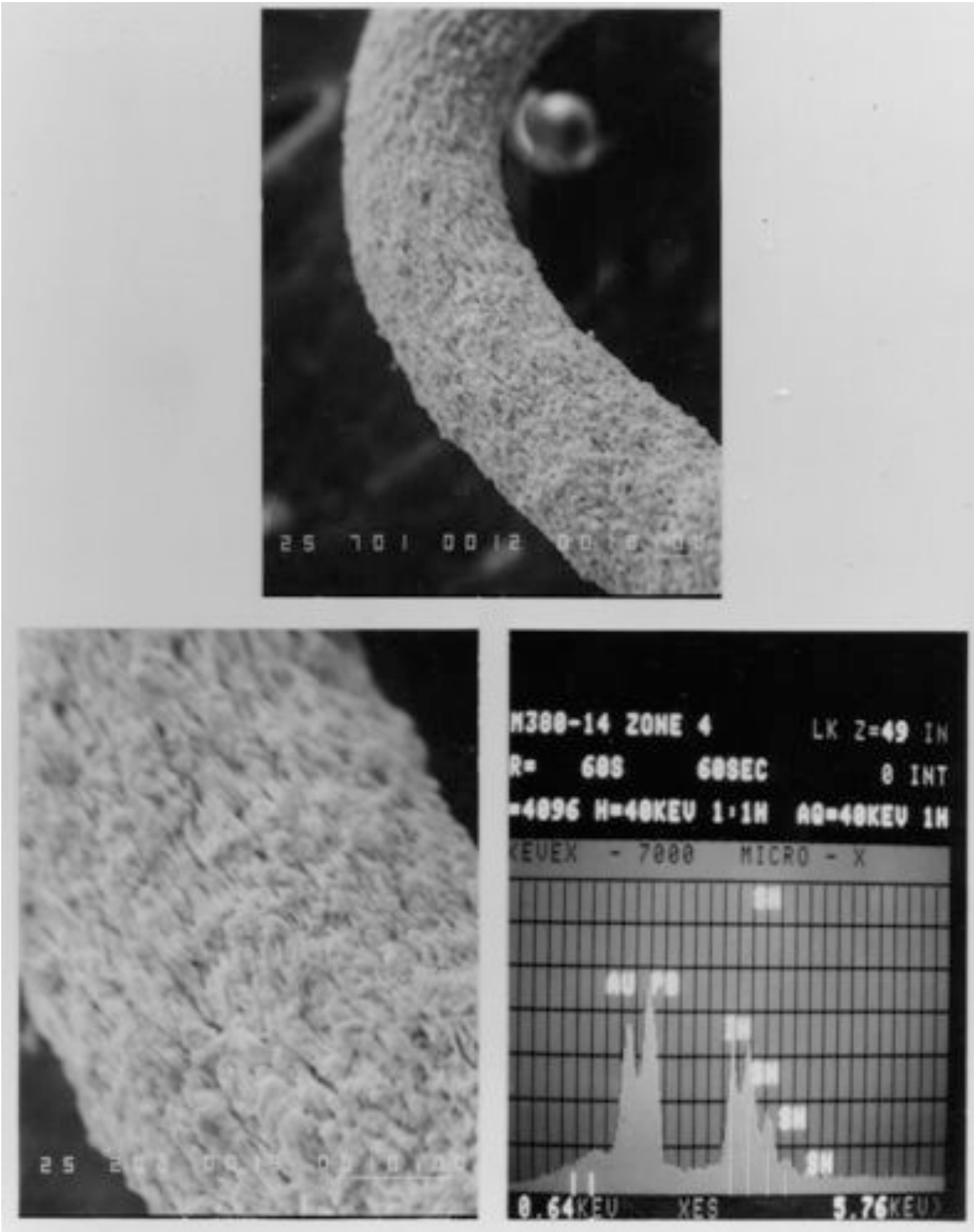

Figure 25. EDS spectrum at locations "4" of figure 21, i.e. on the small diameter (approximately the same as the gold wire's, and clearly not fully dense) "protrusion", the "narrow axial" gold indide growth. Mostly Au and In are present, with some Pb and Sn.

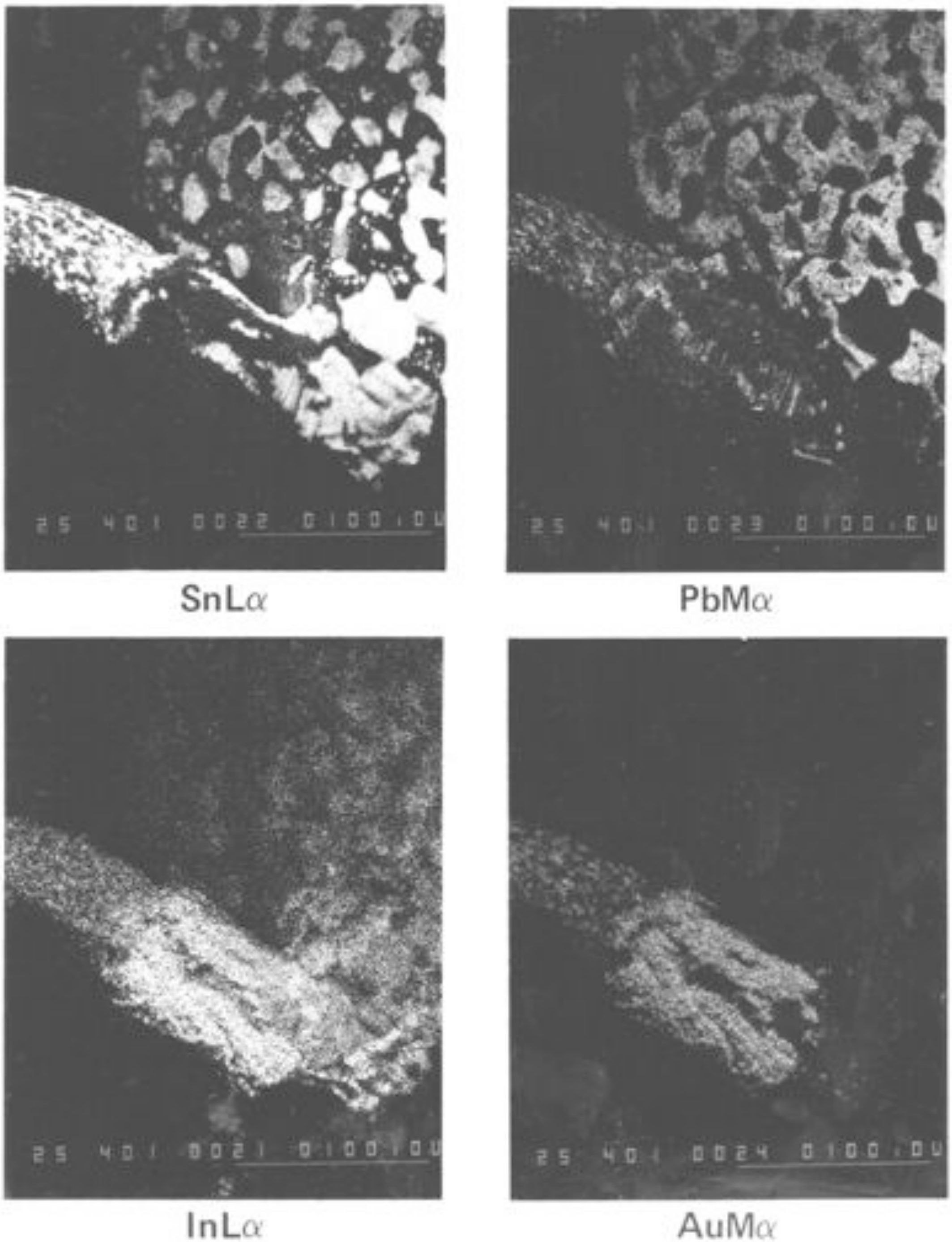

Figure 26. EDS elemental map of the area near the lower solder mound of figure 21, showing that both Pb Sn are present on the surface of both the large diameter and the small diameter "axial" gold indide growth. It implies that the surface diffusivity of Pb and Sn is high at 120°C. Pb and Sn do NOT, however, appear uniformly everywhere, but rather in "speckles".

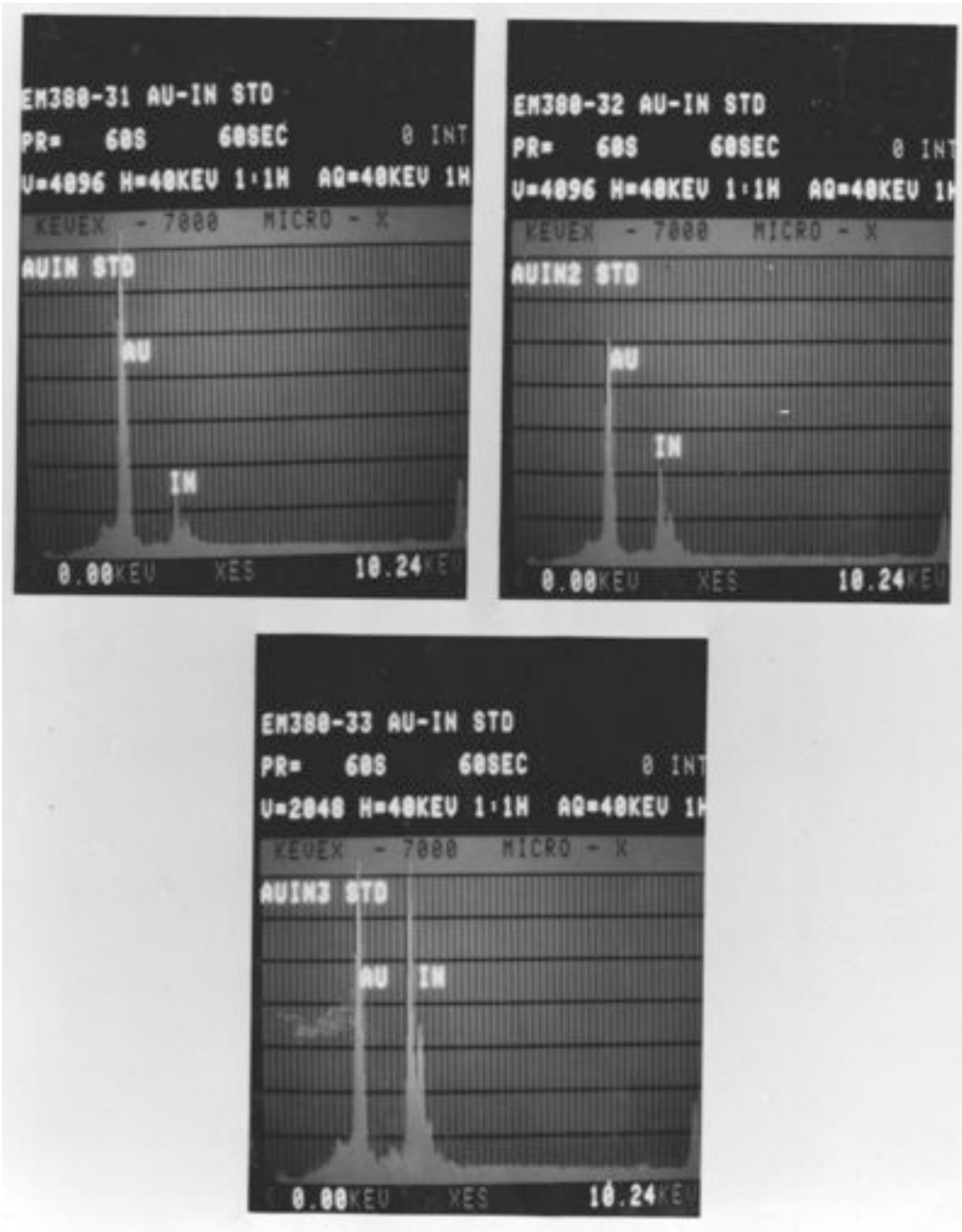

Figure 27. EDS spectra of the calibration standards AuIn, $AuIn_s$ and $AuIn_3$.

B.V.) Summary of observations of the combined "radial/axial" and "axial" reaction"

We describe the gold-indium reaction in gold-wire bridges soldered with PbSnIn (7.5,37,5,25) as follows: The reaction produces $AuIn_2$ and starts radially inside the solder mound and simultaneously axially outside the solder mound (by surface diffusion of indium from the mound) at the point where the wire leaves the mound, forming there in time a protrusion of approximately twice the diameter of the gold wire: the "large diameter axial reaction $AuIn_2$ product". From the angle of the interface between gold and $AuIn_2$ in an axial section through a bridge we conclude that the rate surface diffusion is approximately equal to the rate of the radial reaction.

We calculate that the "radial" reaction inside the solder mound and the formation of large diameter protrusion ("bull nose") outside the solder mound produces NO, or a hardly noticeable resistance change, because the increase in resistance due to the lower conductivity of $AuIn_2$ is compensated for by the larger diameter of the reaction product inside and outside the solder mound. (This is confirmed by comparing original resistance values with values from surveillance samples where complete conversion inside the solder mound has occurred).

Long term experiments with 1.5 mil gold-wire headers at temperatures between 40 and 120°C do, however, produce larger resistance changes (observed for temperatures above 60°C). We demonstrate that this large resistance increase begins when the *Linear Reaction Model* described in part A. predicts that all gold inside the solder mound is converted to $AuIn_2$. We confirm this prediction by simultaneous time lapse photography and resistivity measurements at 120°C, where we demonstrate that the resistivity of the bridge starts to increase rapidly while the "small diameter purely axial $AuIn_2$ reaction" proceeds from the end of the large diameter protrusion along the remainder of the gold-wire. Since to each mole of gold two moles of indium are added to form gold indide, and the density of gold indide is about a factor 2 lower than gold's (9.96 vs. 19.3 g/cm^3) each dx of the gold wire becomes approximately 4.2 dx of "small diameter $AuIn_2$" (about the same diameter of the gold wire), deforming the wire into the contorted shape seen in Figure 19.

We demonstrate by electron dispersive spectroscopy (EDS) that both the "large diameter" and the "small diameter" reaction product is $AuIn_2$. Surprisingly, EDS reveals that both Pb and Sn are present in the "large diameter" and in the "small diameter" reaction product in the experiment at 120°C. This fact implies that both Sn and Pb have high surface diffusion coefficients. EDS, one must point out, samples only the surface of the material, typically less than one micrometer.

The formation of the "small diameter" reaction product and the concomitant rapid increase in resistance has never been observed at low temperature.

Work at the Lawrence Livermore National Laboratory has shown that, although the "bull nose", the "large diameter external $AuIn_2$", has only a negligible effect on the static resistivity of the bridge, it does have a noticeable effect on the explosion dynamics of bridge-wires.